

Canopy influence on trace metal atmospheric inputs on forest ecosystems: Speciation in throughfall

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A B S T R A C T

Atmospheric inputs of selected Trace Metals (TM: Cd, Cu, Ni, Pb, Sb, Zn, as well as Al, Fe and Mn) were studied on six forested sites in France. In order to evaluate canopy interaction with atmospheric inputs, TM were measured in both Open Field Bulk Deposition (BD) and Throughfall (TF). Anthropogenic contribution to BD composition is high for Zn, Cd and Sb, reflecting actual TM emissions trends. Canopy greatly influences precipitation composition, through different processes, including assimilation and leaching by canopy, complexation as well as accumulation/dissolution of dry deposition. TM and Dissolved Organic Carbon (DOC) physical fractionation between colloidal and truly dissolved phases was performed with ultrafiltration. Al, Fe, Pb and Cu are found in the colloidal fraction whereas Cd, Ni, Zn and Sb are mostly in the truly dissolved fraction. Chemical speciation predicted with WHAM-VI shows that in throughfall, Al, Fe, Pb and Cu are almost entirely complexed by DOC, whereas Ni, Cd and Zn are present in average 30% in the free metal ion form. TM present in labile forms (Cd, Ni, Zn) interact with the canopy, are cycled in the ecosystem, and their concentration is either slightly increased or even decreased in throughfall. Sb, Pb and Cu concentration are increased through canopy, as a consequence of dry

1. Introduction

Atmosphere plays a key role in global metal cycles as it receives inputs from many sources and leads to metal dispersion at the Earth scale (Rauch and Pacyna, 2009). Trace Metal (TM: Cd, Cu, Ni, Pb, Sb and Zn) spreading in the atmosphere is induced by natural processes (Nriagu, 1989), as well as anthropogenic activity (Pacyna and Pacyna, 2001). They can be conveyed to long distances (Steinnes and Friedland, 2005) and impact remote ecosystems (Shotyk et al., 1996). Forest ecosystems are particularly sensitive to atmospheric inputs since forest canopy has a large interaction surface with the atmosphere (Leaf Area Index, LAI = 3 to 10 m² m⁻², Ulrich et al., 1995). Interactions between canopy and TM atmospheric inputs include accumulation of dry deposition, direct assimilation or release of elements by canopy (Lovett and Lindberg, 1984; Balestrini et al., 2007). Throughfall (TF) chemical composition thus results from all processes occurring in the phyllosphere. In

order to study canopy influence on atmospheric inputs, a study of open field Bulk Deposition (BD) and TF is usually performed (Lindberg et al., 1986; Probst et al., 1992; Balestrini et al., 1998; Neal, 2002; Rodrigo et al., 2003; Hou et al., 2005b). TM dynamics in throughfall has also been considered in a few studies (Petty and Lindberg, 1990; Nieminen et al. 1999; Rodrigo et al., 2003; Hou et al., 2005b; Itoh et al., 2006). A high influence of forest canopy is generally observed with element specific dynamics since they are not all enriched through forest cover. Indeed, TM environmental pathways, availability and transport or immobilization in the ecosystem compartments, are directly linked to their speciation (Cheng et al., 1994) and to their potential role for the biosphere. While some of the studied trace elements are micronutrients (Zn, Cu, Ni), others (Cd, Sb, Pb) have no known biological role (Peralta-Videa et al., 2009). Only few studies (Hou et al., 2005a; Casartelli et al., 2006) have dealt with TM speciation in throughfall, although it provides useful information on canopy processes. Complexing capacity of DOC to Cu and some other TM (Bi, Sn, Ag) was proved, highlighting the conveying role of DOC for some metals below canopy. However, no study of throughfall speciation (including modeling and physical partitioning approaches) in temperate climate forest ecosystems has already been performed for the elements we propose to study (Cd, Cu, Ni, Pb, Sb and Zn).

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Table 1

Location, soil type, vegetation cover, average precipitation amount of the six studied sites.

Site	Location	Soil type ^a	Vegetation cover (planting age)	Mean annual precipitation (1993–2007) (mm)
EPC 08	Ardennes	Cambic podzol	<i>Picea abies</i> (L.) Karst (50 years)	1399
EPC 63	Puy de Domes	Mollic andosol	<i>Picea abies</i> (L.) Karst (45 years)	1153
EPC 87	Haute-Vienne	Cambic podzol	<i>Picea abies</i> (L.) Karst (45 years)	1399
HET 64	Pyrénées Atlantiques	Eutric cambisol	<i>Fagus sylvatica</i> L. (80 years)	1406
SP 11	Aude	Stagnic luvisol	<i>Albies Alba</i> Mill. (100 years)	1126
SP 57	Vosges	Dystric cambisol	<i>Albies Alba</i> Mill. (100 years)	1380

^a World base reference.

The objectives of the study are to:

- (i) determine TM concentrations in open field Bulk Deposition and Throughfall in six French forest sites,
- (ii) determine TM and DOC physical fractionation between colloidal and truly dissolved phase in throughfall,
- (iii) model TM speciation in all physical fractions,
- (iv) evaluate the main processes controlling metal behavior after interaction with forest canopy.

2. Material and methods

2.1. Studied sites

The study sites (Table 1, Fig. 1) belong to the French RENECOFOR network (Réseau National de suivi à long terme des Ecosystèmes Forestiers, i.e. National Network for the long term Monitoring of Forest Ecosystem), managed by the ONF (Office National des Forêts, i.e. National Forest Board). These sites are part of the European network ICP Forest (level II). They have been chosen because they are representative of a large variety of French forest ecosystems: four main types of soils (podzol, andosol, cambisol and luvisol) and three vegetation types (spruce, *Picea abies* L.; beech, *Fagus sylvatica* L. Karst; and silver fir, *Albies alba* Mill.), all being rather frequently found. The climate is temperate oceanic.

2.2. Sampling procedure and sample treatment

2.2.1. Sampling

For all studied sites, open field Bulk Deposition (BD) and Throughfall (TF) were collected weekly from September 2007 to

October 2008. The sampling procedure used is based on the ICP (<http://www.icp-forests.org/>) protocol, currently applied on these sites. A total of 672 samples were collected. BD was collected in a clearing located next to the forest sites using a 20 cm diameter high density polyethylene (HDPE) funnel linked to a 2 l polypropylene (PP) bottle. The funnel was changed every four weeks and no cleaning of the funnel wall was performed. TF was collected using three HDPE gutters connected to a 20 l HDPE drum. To take into account as much as possible the throughfall variability due to forest cover heterogeneity, the three gutters (0.85 m²) were located at various distances of the stem. Since only two sites were equipped for stemflow collection, stemflow samples were not considered in this study.

All equipment used to collect and store samples were thoroughly rinsed with 1 N HCl and ultra pure MilliQ water. Immediately after sampling, samples were sent to the laboratory in refrigerated tanks and stored in a cold room (4 °C) before being analyzed within a few days.

2.2.2. Chemical analysis

After pH and conductivity measurements, all samples were filtered through a 0.22 µm nitrocellulose filter. Major elements were analyzed on four week volume-weighted composite samples by the ICP-chartered laboratory. Trace Metal analyses were also performed on four week amount-averaged samples. Samples were acidified (2%) with ultra pure HNO₃ prior to ICP-MS (7500 ce, Agilent Technologies) analysis and kept in cold (4 °C) chamber. ¹¹⁵In was used as an internal standard. SLRS-4 (River water certified for trace elements) was used as a reference material on every run and accuracy (recovery > 95%) was checked. Determination limits were <0.5 µg l⁻¹ for Fe and Al, <0.05 µg l⁻¹ for Mn, Ni, Cu and Zn and <0.005 µg l⁻¹ for Cd, Zn and Pb. Dissolved Organic Carbon (DOC) analyses were performed on HCl

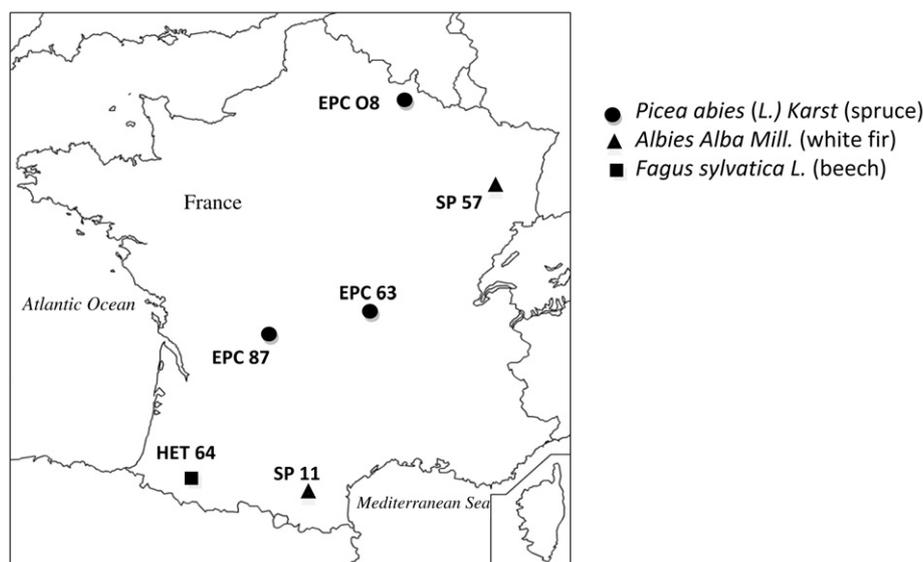


Fig. 1. Location and forest cover types of studied sites.

Table 2
Mean rainfall amount and volume-weighted mean and standard deviation (in brackets) of pH, DOC and TM concentrations measured in open field Bulk Deposition (BD) and Throughfall (TF) on the six studied sites ($n = 14$ for BD and TF) and for all studied sites ($n = 84$ for BD and TF). $R (F_{TF}/F_{DB})$ represents the ratio of TF and BD fluxes.

			EPC 08	EPC 63	EPC 87	HET 64	SP 11	SP 57	All sites
Rainfall amount	BD	mm	1425	1133	1654	1659	972	1212	–
	TF		1090	655	929	959	662	620	–
pH	BD	–	5.18 (0.51)	5.7 (0.41)	5.27 (0.51)	5.18 (0.6)	5.34 (0.61)	4.9 (0.37)	4.34 (0.47)
	TF	–	5.26 (0.48)	5.4 (0.53)	5.46 (0.43)	5.68 (0.43)	5.8 (0.35)	4.95 (0.79)	5.58 (0.57)
	$R (F_{TF}/F_{DB})$		0.42	0.30	0.80	0.42	0.33	0.47	0.4
DOC	TF	mg l^{-1}	6.88 (3.74)	10.27 (4.45)	9.55 (4.4)	2.52 (2.42)	13.48 (7.04)	9.29 (5.25)	8.29 (5.18)
Al	BD	$\mu\text{mol l}^{-1}$	245.7 (219.3)	169.4 (513.8)	115.8 (72.5)	97.4 (122.3)	150.6 (114.2)	124 (97.4)	142 (157)
	TF		699.5 (612.6)	1263.7 (613.6)	1457.1 (1039.1)	259.3 (114.7)	1615.9 (1013.5)	1019.7 (622.5)	1029 (478)
	$R (F_{TF}/F_{DB})$	–	2.2	4.3	7.1	1.9	7.9	4.2	4.3
Mn	BD	$\mu\text{mol l}^{-1}$	58.3 (32.7)	38 (62.8)	36.2 (19.3)	41.6 (66.1)	36.9 (30.8)	50.4 (45.1)	43.6 (27.6)
	TF		2441.4 (1533.7)	1522.7 (1307.5)	916.9 (568.6)	752.9 (883.9)	749.3 (353.9)	6050 (2493.6)	1946.2 (1336.6)
	$R (F_{TF}/F_{DB})$	–	32.0	23.1	14.2	11.5	14.3	61.3	27.1
Fe	BD	$\mu\text{mol l}^{-1}$	74.7 (67.4)	43.1 (141.9)	36.4 (20.7)	33.1 (53.3)	34.7 (31.5)	37.3 (44)	42.7 (44.3)
	TF		183 (110.1)	282.9 (139.6)	173.6 (121.2)	85.1 (27.6)	369.2 (200.9)	197.9 (92.9)	206.9 (71.9)
	$R (F_{TF}/F_{DB})$	–	1.9	3.8	2.7	2.2	8.2	2.7	2.9
Cd	BD	nmol l^{-1}	0.798 (1.258)	0.543 (1.044)	0.164 (0.064)	0.198 (0.136)	0.197 (0.163)	0.246 (0.266)	0.352 (0.348)
	TF		0.442 (0.459)	0.228 (0.081)	0.155 (0.119)	0.171 (0.202)	0.415 (0.258)	0.515 (0.225)	0.314 (0.0186)
	$R (F_{TF}/F_{DB})$	–	0.4	0.2	0.5	0.6	1.6	1.1	0.5
Cu	BD	nmol l^{-1}	13.12 (8.09)	10.72 (7.2)	10.43 (4.8)	9.27 (15.48)	13.47 (13.71)	7.25 (5.72)	10.33 (5.90)
	TF		19.22 (14.17)	27.12 (11.68)	32.13 (20.19)	13.75 (9.51)	34.84 (25.1)	22.95 (14.57)	24.46 (10.29)
	$R (F_{TF}/F_{DB})$	–	1.1	1.5	1.7	1.0	1.9	1.6	1.4
Ni	BD	nmol l^{-1}	8.28 (5.14)	5.76 (12.22)	5.62 (2.08)	4.23 (2.84)	11.25 (14.53)	4.51 (3.17)	6.25 (5.23)
	TF		9.92 (8.96)	8.21 (3.45)	6.99 (4.07)	7.73 (8.69)	13.39 (9.06)	11.71 (5.48)	9.46 (4.05)
	$R (F_{TF}/F_{DB})$	–	0.9	0.8	0.7	1.2	0.9	1.3	0.9
Pb	BD	nmol l^{-1}	3.85 (2.84)	1.00 (0.86)	1.00 (0.63)	1.2 (1.21)	1.06 (0.72)	2.04 (3.21)	1.70 (1.05)
	TF		12.84 (9.32)	15.49 (10.58)	18.99 (16.3)	2.96 (1.36)	34.55 (20.07)	6.94 (5.42)	15.26 (8.59)
	$R (F_{TF}/F_{DB})$	–	2.6	8.9	10.7	1.6	22.3	1.7	5.4
Sb	BD	nmol l^{-1}	1.05 (0.65)	0.44 (0.19)	2.07 (4.02)	1.13 (2.45)	5.31 (12.06)	0.57 (1.06)	0.15 (0.22)
	TF		5.99 (3.08)	7.46 (4.82)	12.61 (4.72)	8.13 (3.88)	9.80 (4.87)	14.53 (9.19)	9.50 (3.57)
	$R (F_{TF}/F_{DB})$		4.4	9.9	3.4	4.3	1.5	12.9	3.8
Zn	BD	nmol l^{-1}	194.9 (127.3)	628.6 (862.4)	120.8 (77.9)	450.9 (566.1)	336.1 (409.9)	217.5 (248.9)	310.8 (292.7)
	TF		298.9 (396.4)	270.2 (142.7)	217.2 (138.8)	154.2 (82.1)	207 (161.6)	507.1 (275.2)	265.4 (161.3)
	$R (F_{TF}/F_{DB})$	–	1.2	0.2	1.0	0.2	0.4	1.2	0.5

(ultrapure, 11 M) acidified samples kept in glass bottles with a Shimadzu apparatus. Quantification limit was 0.7 mg C l^{-1} . SUVA_{254} (Specific UV Absorbance at 254 nm) was determined on the same samples with a UV spectrophotometer (Secoman UVi-lightXT5). The Specific UV Absorbance ($\text{SUVA}, 1 \text{ mg}^{-1} \text{ m}^{-1}$) was calculated as follows using the approach of Weishaar et al. (2003):

$$\text{SUVA} = \frac{A^{254} \cdot 1000}{b \cdot [\text{DOC}]} (1 \text{ mg}^{-1} \text{ m}^{-1})$$

where A^{254} is the sample absorbance at 254 nm (non-dimensional), b is the thickness of the measurement tank (m) and DOC is in mg l^{-1} . The specific UV absorbance is used as an estimate of the aromaticity of DOM (Weishaar et al., 2003).

2.2.3. Physical fractionation

In order to isolate the colloidal fraction ($1 \mu\text{m} - 1 \text{ nm}$ (IUPAC)) in throughfall, two filtration steps (1.2 and $0.2 \mu\text{m}$), followed by one step of ultrafiltration (3000 Da) were performed during one month (September 2008). Filtration steps (1.2 and $0.2 \mu\text{m}$) were performed as routine filtration with surfactant free nitrocellulose filters, previously rinsed with MilliQ water and a small amount of the sample, which was discarded. Ultrafiltration step (3000 Da) was performed with 15 ml Millipore ultrafiltration devices using a Beckman Aventi J26 XPI centrifuge with swinging bucket at $3000g$ for 20 min . To avoid TM and DOC contamination of the samples, each ultrafiltration device was rinsed with $\text{HCl } 1 \text{ M}$ and MQ water

three times before use. Similarly to the samples, the same ultrafiltration procedure was done with MilliQ water and showed no evidence of contamination. No TM adsorption on these ultrafiltration devices was evidenced (Pourret et al., 2007).

This protocol allowed to isolate three fractions: a Coarse Colloidal (CC) one, comprised between 0.22 and $1.2 \mu\text{m}$, a Fine Colloidal (FC) one, comprised between 3 kDa and $0.22 \mu\text{m}$ and a Truly Dissolved (TD) fraction, under 3 kDa .

2.2.4. Speciation simulation using WHAM-VI

WHAM-VI (Tipping, 1998) was used to evaluate chemical speciation of metals in throughfall. WHAM-VI is a geochemical computer code that describes interaction between metallic cations and several ligands, mainly organic matter in natural waters. Binding is described by discrete sites, taking into account electrostatic interactions. Input data were pH, concentrations of major cations (Ca, Na, K, Mg), and trace elements (Cr, Cu, Ni, Pb, Sb and Zn), major acid anions concentrations (Cl, SO_4 and NO_3). Speciation simulations showed that less than 1% Fe and Al hydroxides were detected in throughfall. Total measured concentrations of Fe and Al were thus used as input values. Measured DOC in TF was considered, as in previous studies (Tipping et al., 2003; Pampura et al., 2007) to be constituted by 65% of “active” fulvic acids with respect to cation binding. WHAM-VI was developed for natural freshwater and soil solution. We assume that throughfall DOM has the same binding properties to cations as soil solution or freshwater fulvic acids. In fact, it was observed on RENECOFOR sites that DOM acid–base

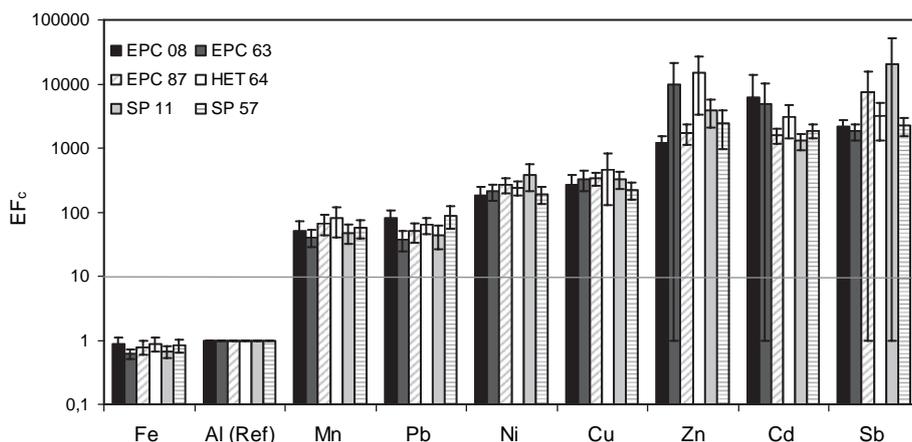


Fig. 2. Crustal Enrichment Factor (EF_c) in open field Bulk Deposition (BD) for the considered elements for the different studied sites. Al is taken as a reference.

properties were similar in soil solution and throughfall (Fillion-Guigues, et al., 1999). Moreover, DOC in TF can contribute to 30% of the DOC fluxes in forest soil solution and contains similar organic molecules like phenolics and carboxylic acids (Hou et al., 2005a).

Results are based on two data sets: (i) samples from the annual survey (14 samples for each sites representing the volume-weighted average of four week sampling), for a total of 84 samples for both BD and TF. (ii) A limited number of samples used for physical partitioning (Coarse Colloidal: CC, Fine Colloidal: FC and Truly Dissolved: TD after ultrafiltration). Data from 3 to 5 replicates on each site were obtained with a total of 24 samples.

3. Results

3.1. TM concentrations in bulk open field precipitation and throughfall

Summary information on rainfall amount, as well as pH, DOC, major (Al, Mn and Fe) and trace elements' concentrations is presented in Table 2.

Rainfall amount was modified through the canopy (Viville et al., 1993). Interception represented 20–50% of the rainfall amount for the studied sites, which corresponds to the average value for

temperate French forests (Ulrich et al., 1995). BD was slightly acidic (mean pH is 4.3 ± 0.5) and through the canopy, mean precipitation pH slightly increased (mean pH is 5.6 ± 0.6). Thus, a net decrease in proton fluxes was observed in all studied sites (as indicated by the R ratio in Table 2).

Since concentrations were very low (usually below 1 mg l^{-1}), DOC concentration in BD was not systematically measured. DOC concentration was greatly increased in throughfall. No significant difference (Kruskall–Wallis test, $\alpha = 0.05$) between DOC concentration according to tree species was noticed, except for the beech site, where DOC concentration was significantly lower than for coniferous sites.

TM concentrations were similar to measurements from rural areas (Galloway et al., 1982; Hou et al., 2005b). Concentration variability was high for a single site, thus only few significant differences between the different sites were observed (Kruskall–Wallis test, $\alpha = 0.05$). Concentrations for Pb in EPC 08 and Zn in HET 64 were significantly higher than in other sites. Environmental regional characteristics including climatic and atmospheric pollution background can explain these differences.

In TF, no significant differences in concentrations between sites were observed (Kruskall–Wallis test, $\alpha = 0.05$), except for Al, Fe and Pb, which were significantly less concentrated on HET 64.

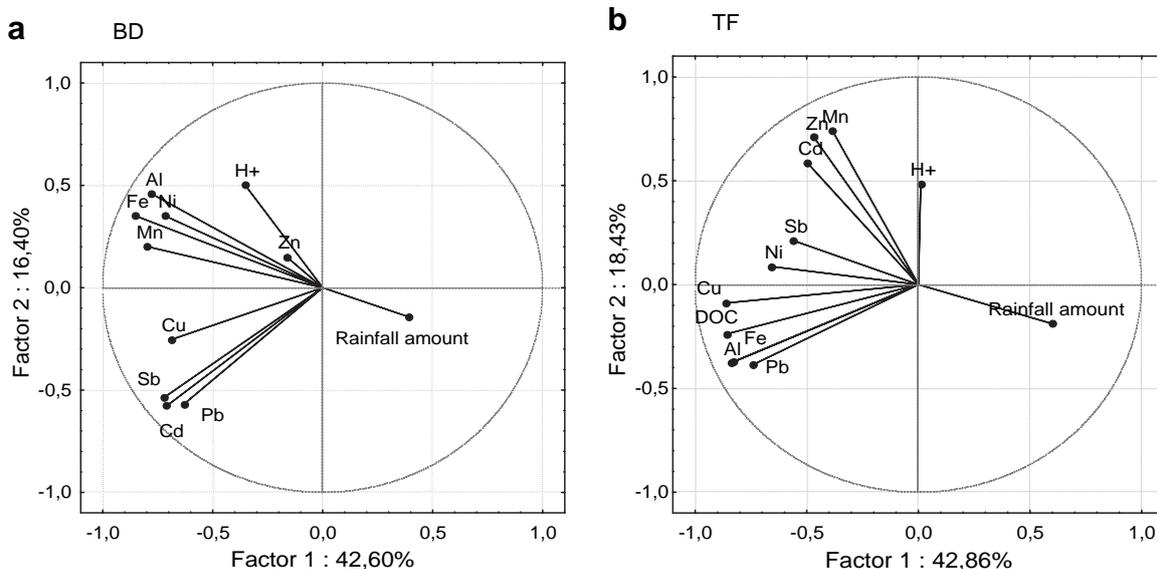


Fig. 3. PCA of element concentrations in BD and TF samples. (a) BD, (b) TF.

Table 3

PCA of studied elements concentrations in BD and TF. Variable contribution to the first three factors (F1, F2, F3).

Factor contribution (%)	OFF			TF		
	F1	F2	F3	F1	F2	F3
	43	16	12	43	18	9
Rainfall amount	0.392	-0.142	-0.418	0.602	-0.189	-0.254
H ⁺	-0.353	0.503	-0.375	0.011	0.485	0.208
DOC	-	-	-	-0.859	-0.238	0.104
Al	-0.780	0.460	-0.200	-0.837	-0.376	0.116
Mn	-0.797	0.201	-0.095	-0.384	0.740	0.224
Fe	-0.854	0.352	-0.216	-0.830	-0.373	-0.011
Ni	-0.717	0.351	0.306	-0.659	0.087	0.158
Cu	-0.689	-0.254	0.410	-0.862	-0.089	-0.201
Zn	-0.164	0.151	0.737	-0.469	0.712	-0.306
Cd	-0.709	-0.577	0.012	-0.495	0.584	-0.533
Sb	-0.720	-0.536	-0.112	-0.560	0.212	0.554
Pb	-0.631	-0.570	-0.262	-0.741	-0.386	-0.335

Elemental concentrations were generally higher in TF than in BD. However, concentration modifications through canopy were element specific. As rainfall amount was reduced through canopy, modifications induced by canopy were investigated by flux ratios (*R*, Table 2) rather than concentration ratios. Some differences appeared between sites. Mn fluxes were the most increased through forest canopy (always more than 10 times). Al, Pb, Fe and Sb fluxes were also greatly influenced by the canopy, with average fluxes increase from 2.9 for Fe to 5.4 for Pb. For, Cd, Cu, Ni and Zn, depending on sites, concentrations were slightly increased or even decreased through the canopy. Even if a similar behavior for each element can be identified, differences between sites can be important. For example, the flux increase through the canopy is particularly high on SP 11 site for Fe ($R=8.2$) and Pb ($R=22.3$) and on SP 57 for Sb ($R=12.9$) (see Table 2). A lower flux increase is noticed for Al, Cu and Pb on HET 64 site. However, the influence of tree species could not be highlighted from these measurements. Numerous factors, including tree species and therefore canopy structure, tree density in the plot as well as local meteorology can explain these differences between sites.

3.2. Crustal enrichment factor for studied elements

The crustal Enrichment Factor (EF_c) (Duce et al., 1975) of an element in precipitation (BD) is the ratio of the concentration of this element to the concentration of a reference element (Al), to the same ratio in the Upper Continental Crust (UCC; McLennan, 2001).

The aim is to discriminate natural and anthropogenic sources in precipitation. It is defined as:

$$EF_c = \frac{(X/Al)_{OFF}}{(X/Al)_{UCC}}$$

The results are given in Fig. 2 for the six studied sites. No significant differences were observed for EF_c between studied sites. For Fe, EF_c was close to 1, indicating a crustal origin for this element, with no anthropogenic input. For the other elements (except Al which is the reference), EF_c was always higher than a factor of 10. In BD, due to local variation in crustal composition, a limit of 10 rather than 1 is preferred (Poissant et al., 1994) to consider a significant anthropogenic enrichment. A limit of 100 (Steinnes and Friedland, 2005) or 500 (Poissant et al., 1994) is chosen to discriminate moderate and high enrichments. With those references, a moderate to high enrichment is considered for Mn, Pb, Ni and Cu and a very high enrichment for Cd, Zn and Sb, indicating a strong anthropogenic influence.

3.3. Correlation analysis

Principal components analysis was performed on element concentrations in BD and TF (Fig. 3a, b and Table 3). Samples from all sites were included. The variables included in the analysis were TM (Cd, Cu, Ni, Pb, Sb and Zn), rainfall amount and pH in BD and TF. Two analyses were performed for TF, without and with DOC concentrations (the latter only shown in Fig. 3b). Both analyses yield similar results.

3.3.1. Bulk deposition

In BD, most of the elements (Cd, Cu, Ni, Pb, Al, Fe, Mn,) contributed to factor 1 (43% of the data variance) and presented a similar behavior with a negative correlation with rainfall amount (Fig. 3a, Table 3). Groups of elements presented different associations with factor 2. Al, Fe, Mn and Ni were positively linked to each other, whereas Cd, Pb, Sb and to a lesser extent Cu form another group negatively correlated with the second factor (Fig. 3a). Zn was less significantly related to other elements and was well related to factor 3 (Table 3). These associations indicate similar sources, and/or geographic origins, and/or chemical affinity in the atmosphere (Poissant et al., 1994).

3.3.2. Throughfall

In throughfall, correlations between elements were modified with respect to OFF (Fig. 3a and b): associated elements in BD are split and other groups were formed. Rainfall amount was

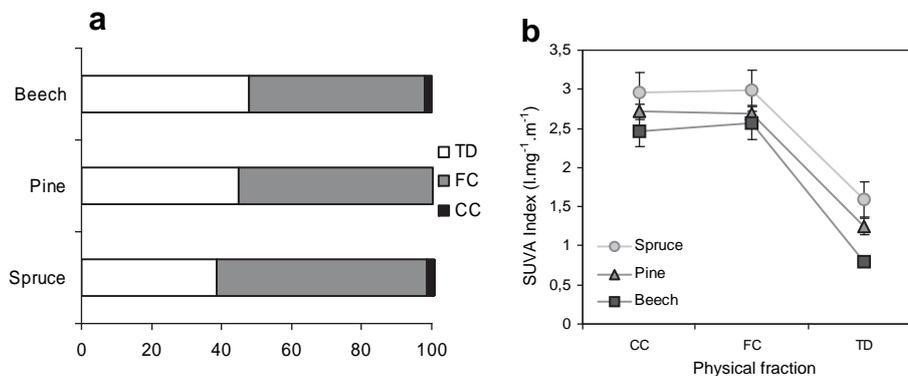


Fig. 4. (a) Physical partitioning of DOC in TF between Coarse Colloidal (CC), Fine Colloidal (FC), and Truly dissolved (TD) fractions; (b) measured values of SUVA index in the different physical fractions according to forest cover.

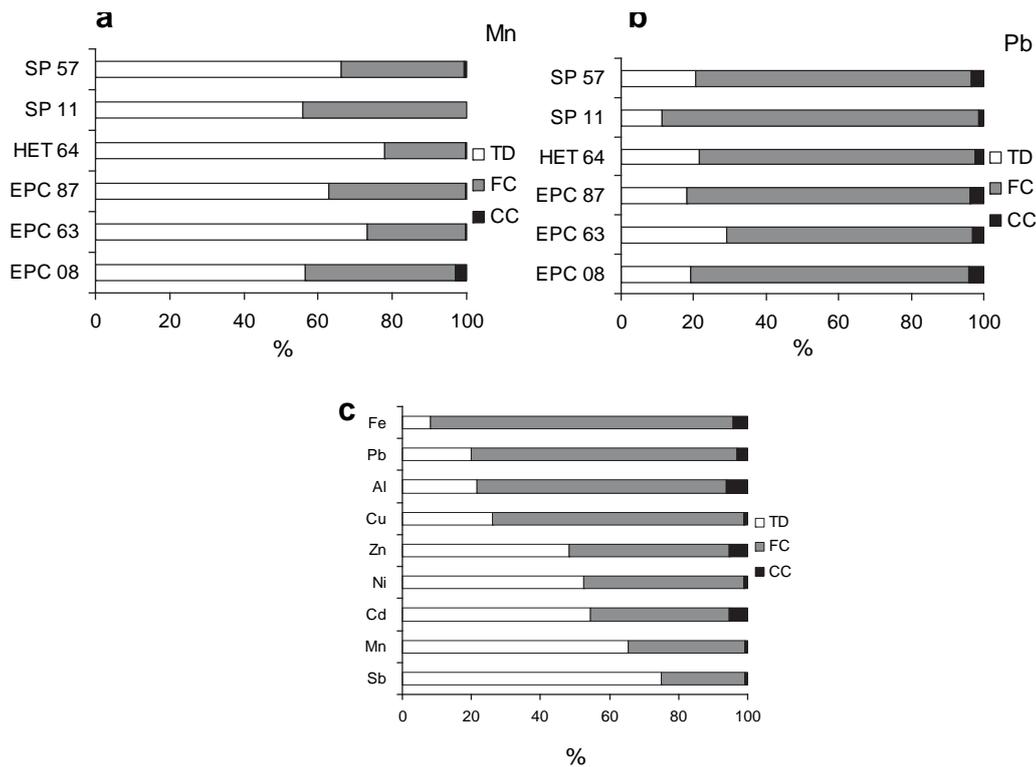


Fig. 5. Physical fractionation of studied TM between Coarse Colloidal (CC), Fine Colloidal (FC), and Truly dissolved (TD) fractions. Detailed results on the six studied sites for Mn (a) and Pb (b) and mean results on the six studied sites for all elements (c).

a significant variable, which was negatively correlated to the element concentrations. Rainfall amount, DOC, Al, Fe, Cu, Ni and Pb contributed to factor 1 (43% of the variance). Mn, Zn and to a lesser extent Cd and H^+ were related to factor 2. Al, Fe, Cu and Pb were related to each other and to DOC, whereas Cd, Zn and Mn constituted another group. Ni and Sb were not closely related to other elements, and were located in-between.

3.4. Throughfall chemistry

3.4.1. Physical fractionation of DOC

Physical fractionation of DOC in throughfall was similar for the three studied forest cover types (Fig. 4a). DOC was composed by

about 50% of fine colloidal molecules and 50% of low molecular weight (<3 kDa) organic molecules. SUVA index values were similar regarding forest cover (Fig. 4b), although lower values were measured in the beech site. Throughfall SUVA index values were in the range (1–6) described for natural waters (Weishaar et al., 2003). However, SUVA indexes depended on the physical fraction. In the colloidal fraction (coarse and fine colloids), comparable SUVA index values were observed. On the opposite, a 50% drop in SUVA index values was observed after UF step. The percentage of aromaticity (aromaticity (%) = $6.52 \times \text{SUVA} + 3.63$; Weishaar et al., 2003) derived from the SUVA index decreased from a mean value of 21% in colloidal fraction to 11% for the low molecular weight organic molecules.

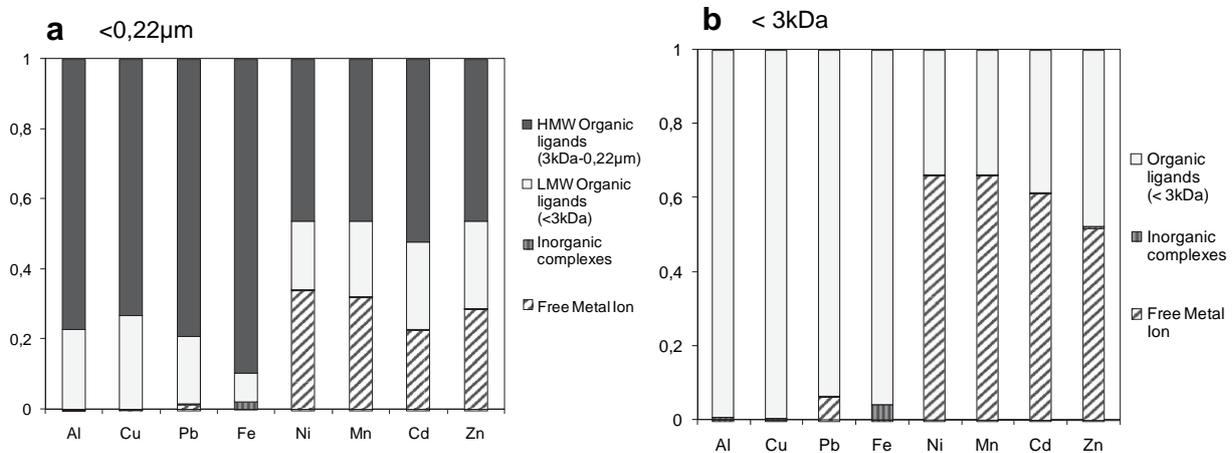


Fig. 6. TM speciation predicted by WHAM-VI in 0.22 μm (a) filtered samples and ultrafiltered (<3 kDa) samples (b). In figure (a), the organic ligands in the 0.22 μm filtered samples have been divided in LMW (<3 kDa) and HMW (>3 kDa) complexes.

Table 4

Correlation coefficients between TM and DOC in throughfall depending on the physical fraction: <1.2 μm ; <0.22 μm and <3 kDa. $n=24$. "0.2 μm (all samples)" refers to the annual survey samples ($n=84$). Bold: $p < 0.001$; in italic: $p < 0.05$; n.s. = non-significant.

	1.2 μm		0.2 μm		0.2 μm (all samples)		<3000 Da	
	<i>r</i>	<i>p</i>	<i>r</i>	<i>p</i>	<i>r</i>	<i>p</i>	<i>r</i>	<i>p</i>
Al	0.860	<0.0001	0.815	<0.0001	0.809	<0.0001	0.592	<0.01
Mn	<i>0.031</i>	n.s.	<i>0.147</i>	n.s.	<i>0.260</i>	<0.05	<i>0.131</i>	n.s.
Fe	0.890	<0.0001	0.898	<0.0001	0.826	<0.0001	<i>0.337</i>	n.s.
Ni	0.814	<0.0001	0.770	<0.0001	0.570	<0.0001	0.755	<0.0001
Cu	0.830	<0.0001	0.776	<0.0001	0.645	<0.0001	<i>0.095</i>	n.s.
Zn	<i>-0.031</i>	n.s.	<i>0.375</i>	n.s.	<i>0.151</i>	n.s.	<i>0.142</i>	n.s.
Cd	<i>0.003</i>	n.s.	<i>0.336</i>	n.s.	<i>0.269</i>	<0.05	<i>0.179</i>	n.s.
Pb	0.725	<0.0001	0.723	<0.0001	0.655	<0.0001	<i>0.403</i>	n.s.
Sb	<i>0.268</i>	n.s.	<i>0.336</i>	n.s.	<i>0.393</i>	n.s.	<i>0.315</i>	n.s.

3.4.2. Physical fractionation of TM

Physical partitioning of the studied elements between Truly Dissolved (<3000 Da), Fine Colloids (3000 Da–0.2 μm) and Coarse Colloids (0.2–1.2 μm) is presented in Fig. 5. The studied elements were mainly found in the ultrafiltered and fine colloidal fractions. The physical fractionation of elements was not significantly different between sites (Fig. 5a and 5b, Mn and Pb, for examples). Mean values for the six studied sites were presented for all studied elements (Fig. 5c). The coarse colloidal fraction (0.2–1.2 μm) constituted less than 6% of the total concentrations for all the studied elements. Physical fractionation between colloidal fraction and truly dissolved phase greatly depended on the element. For Fe, Pb, Al and Cu, the ultrafiltered phase represented less than 26% of the total concentration, whereas the fine colloidal fraction was the dominant fraction (from 72% Cu to 87% Fe). Zn, Ni, Cd, Mn and Sb were mainly found in truly dissolved phase (from 48% Zn to 72% Sb). The fine colloidal fraction thus represented less than 50% of the total concentration, with a mean value in the range of 46% for Zn to 24% for Sb.

3.4.3. Throughfall speciation predicted by WHAM-VI

The results of speciation calculations performed on throughfall for filtered (<0.22 μm) and ultrafiltered (<3 kDa) samples, are summarized in Fig. 6a and b, respectively. In ultrafiltered samples, active carbon content was adjusted so that Free Metal Ion (FMI) concentrations of the studied elements predicted in the filtered (<0.22 μm) and ultrafiltered (<3 kDa) samples match. The adjustment was done by minimizing the square of the difference between FMI concentration predicted in filtered and ultrafiltered solution, for each sample. The percentage of active carbon was then reduced in the ultrafiltered samples compared to filtered samples and finally represented from 100 to 23% of the active carbon considered in the filtered samples. The proportions of free metal ion, inorganic complexes (hydroxides, Cl, SO_4 and CO_3 complexes) and organic complexes in 0.22 μm filtered and ultrafiltered samples are indicated for the studied elements (respectively, Fig. 6a and b). Al, Cu and Pb were almost completely complexed by Fulvic Acids in both fractions, whereas in filtered samples (<0.22 μm), between 20 and 40% of Ni, Zn, Cd and Mn were present as Free Metal Ion (FMI).

In the filtrate (<0.22 μm), the organic complexed fraction of TM could be divided in two distinct fractions (Fig. 6a): Low Molecular Weight (LMW) organic complexes found in the ultrafiltered fraction (<3 kDa) and High Molecular Weight (HMW) for the complexes comprised between 3 kDa and 0.22 μm . HMW material is the main binding agent for all studied elements. About 80% to 90% of Al, Fe, Pb and Cu and 45 to 50% Mn, Zn, Ni and Cd were complexed by HMW organic complexes.

3.4.4. Relationship between TM and DOC

The relationship between TM and DOC was investigated considering the three size fractions (Coarse Colloids, Fine Colloids and Truly Dissolved) separately for the set of samples which were ultrafiltered. Correlation analysis was also performed on the annual survey samples, filtered at 0.22 μm . Correlation coefficients between TM and DOC for the three fractions are reported in Table 4.

Cd, Mn, Sb and Zn concentrations were not correlated to DOC in any fraction, except Cd, which was weakly but significantly related with DOC in the 0.22 μm filtered samples. Al, Fe, Cu, Pb and Ni were significantly and positively correlated with DOC in colloidal fractions (coarse and fine). Except for Ni (and to a lesser extent Al), the association with DOC was modified in the ultrafiltered fraction. No significant relationship between DOC and Fe, Pb and Cu was observed in this fraction.

4. Discussion

4.1. Influence of DOC on TM speciation in throughfall

4.1.1. DOC origin and composition in throughfall

DOC concentration measured in TF is always higher than DOC concentration in BD (Fillion-Guigues et al., 1999; Peichl et al., 2007). Organic carbon in throughfall comes from foliar leaching (Qualls et al., 2000), microbiological as well as herbivore activity in the phyllosphere (Michalzik and Stadler, 2005). In throughfall, DOC concentration is mainly related to rainfall amount and phytophagous insect activity (Kindlmann and Stadler, 2004).

In this study, no influence of tree species on DOC chemistry in TF was evidenced, as previously observed for acid–base properties (Fillion et al., 1998). In TF, DOC was formed by 50% of HMW (3 kDa–1.2 μm) molecules and 50% of LMW (<3 kDa) molecules. Aromaticity content was higher (around 20%) for the HMW molecules as observed in the soil solution (Pédrot et al., 2008). Indeed the aromaticity in TF is related to the presence of polyphenolic compounds such as tannins (Makkar et al., 1991).

4.1.2. Reactivity of DOC with TM in TF

This study showed that DOC partially or totally controls TM speciation in TF. In soil solution, pH is often the main parameter that governs TM speciation (Sauve et al., 2000; Gandois et al., in press). In the studied throughfall solutions, pH was slightly acidic and its variation range was very low (5.26 ± 0.40), whereas DOC concentration was high ($10 \pm 5 \text{ mgCl}^{-1}$). Moreover, DOC in TF is expected to bear carboxylic and phenolic groups that can complex TM (Hou et al., 2005a). Studied elements showed different affinity for DOC, Mn and Sb having the lowest affinity, as no significant relationship between these element concentrations and DOC was observed, although according to speciation calculation, up to 50% of Mn was associated to DOC. Sb speciation could not be predicted with WHAM-VI but physical fractionation showed that Sb was mostly present in the truly dissolved phase, as observed in rivers and soil solutions (Pokrovsky et al., 2006). Sb is negatively charged in natural waters as it hydrolyzes easily and is expected to present a weak affinity for natural organic matter (Filella et al., 2002). Cd and Zn were not correlated with DOC (Table 4) and only partly associated to DOC as predicted by WHAM-VI. Speciation calculations showed that Fe, Al, Cu, Pb were entirely complexed by DOC in TF, and significant correlation between these elements and DOC were observed in colloidal fraction of TF (Fig. 7). Correlation between Fe and DOC has already been observed in *Quercus Myrtilifolia* (Hou et al., 2005a). In the truly dissolved fraction, Al and Ni were the only elements correlated with DOC. For Ni, a similar relationship was observed in all phases (Fig. 7d), whereas for Al (Fig. 7e), the slope in the ultrafiltered (<3 kDa) samples was

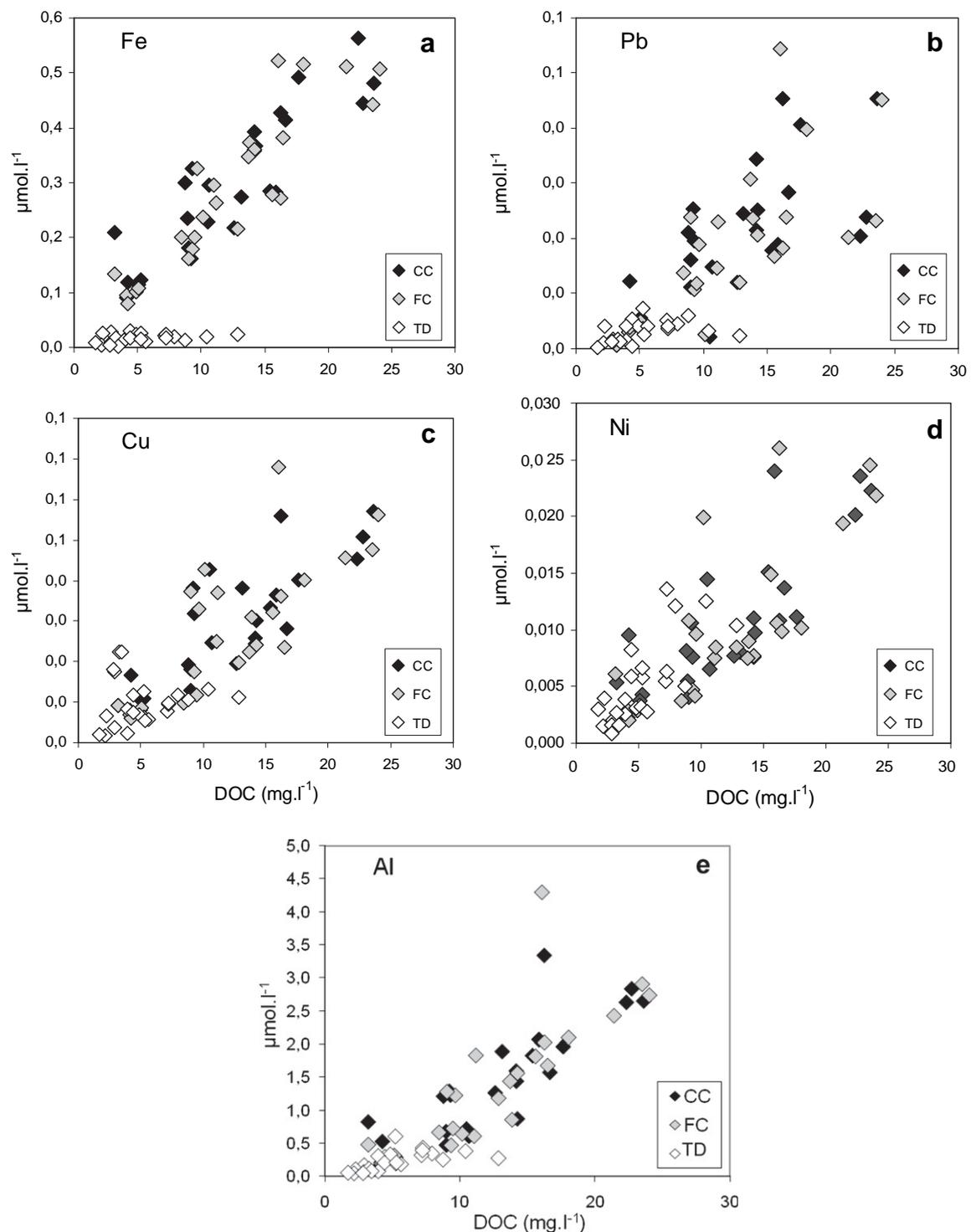


Fig. 7. Relationships between TM and DOC concentrations in the different throughfall fractions (CC: Coarse colloids, FC: Fine colloids, TD: Truly Dissolved). (a) Fe, (b) Pb, (c) Cu, (d) Ni, (e) Al.

lower, which means that less Al was complexed by the same amount of DOC after ultrafiltration. DOC in ultrafiltered samples was less reactive to TM, in agreement with adjustments that were made for WHAM speciation calculation. HMW organic molecules were found to be the most dominant complexing agents for all studied elements. Thus Fe, Al, Pb and Cu were mainly found in the fine colloidal fraction, associated with the most reactive DOC. High concentrations of total phenolics (aromatic species) are related to high copper complexing capacity in TF (Hou et al., 2005a).

4.2. Canopy influence on atmospheric inputs

4.2.1. Origin of trace elements in open field atmospheric precipitation

For all studied elements, except Fe and Al, anthropogenic activities contributed to BD composition, as suggested by calculated EF_c . Concentrations of all elements were negatively correlated with rainfall amount, indicating that “wash-out” processes (i.e. below the cloud scavenging of particles) might be the

dominant one for rainwater composition modification (Poissant et al., 1994). Nevertheless, various groups of elements could be distinguished. Mn and Ni were associated with Al and Fe in BD and had a moderate EF_c indicating a major natural origin. Soil derived dust might account for over 50% of Mn and 30% of Ni emissions in the atmosphere (Nriagu, 1989). Non-ferrous metal production (Cd, Cu, Pb and Zn), as well as stationary fossil fuel combustion (Mn, Ni, Sb), emit substantial amount of metal to the atmosphere (Pacyna and Pacyna, 2001). Combustion of leaded gasoline has been banned since 2000 in Europe, but at a global scale, combustion of leaded and low-leaded gasoline is still the major source of atmospheric Pb emissions, contributing to about 74% to the total anthropogenic emissions (Pacyna and Pacyna, 2001). For the highly enriched elements (Cd, Zn and Sb), waste incineration might be an important source, although emission inventories have to be improved (Pacyna and Pacyna, 2001). Recent increase of Sb emission has been observed (Krachler et al., 2005).

4.2.2. Specific behavior of TM in throughfall

Precipitation composition was highly modified through the canopy. These modifications resulted from washoff of dry deposition, as well as uptake and release of elements by the canopy and associated microflora (Lovett and Lindberg, 1984). The associations between elements in BD reflecting a similar origin or reactivity in the atmosphere were completely modified under the canopy (Fig. 3a and b). TM concentration and speciation in TF were the result of BD composition and its interaction with canopy. TM speciation in TF is thus a useful tool to understand canopy processes.

4.2.2.1. Release and assimilation by forest canopy. A net consumption of proton through forest canopy was observed in all studied sites as indicated by the values of the flux ratios (see Table 2). This pattern is opposite to what was observed in the 80s, especially in the north-east of France, where a proton flux increase was measured in throughfall (Probst et al., 1992). This change is linked to a decrease in precipitation acidity as observed in other places in Northern hemisphere (Burns et al., 2008) and Europe (Cooper and Jenkins, 2003) related to sulfur emissions decrease. Proton consumption can be attributed to base cation buffering processes and ion exchange, leading to cation leaching from canopy (Lindberg et al., 1986; Staelens et al., 2008).

Mn was the most enriched element in TF (Table 2b). In TF, Mn was mainly in the truly dissolved fraction, as FMI (30%), and associated with LMW organic molecules. Mn was thus highly labile in TF and its high enrichment in TF has already been attributed to internal cycling (Petty and Lindberg, 1990).

In BD, Ni, Zn and Cd came probably from different sources, with a more important anthropogenic contribution for Zn and Cd (as indicated by EF_c) than for Ni (clearly associated to terrigenous elements Al, Fe). On the opposite, they presented a comparable behavior in TF, with a slight concentration and flux increase or decrease under canopy (Table 2). Furthermore, in TF, Cd and Zn were significantly correlated with Mn, which is highly leached from canopy. This indicated that these elements were cycled in the ecosystem. Nevertheless, Ni and Zn are micronutrients but Cd has no known biological role, although Mn and Zn substitution by Cd in living cells has been observed (De Baar and La Roche, 2003). Cd, Zn and Ni were present in TF as labile (small organic molecule complexes) and available (FMI) species and, contrary to Mn, their fluxes slightly changed or even decreased in TF suggesting that direct assimilation by foliar surface and related living organism was more important than recreation processes (Petty and Lindberg, 1990; Rodrigo and Avila, 2002; Hou et al., 2005b).

4.2.2.2. Dissolution of dry deposition. In BD, Al, Fe, Cu and Pb had different origins. Al and Fe were naturally present in precipitation. Pb and Cu were moderately enriched in BD and they might have both terrigenous and anthropogenic origin (Nriagu, 1989; Pacyna and Pacyna, 2001). In TF, Pb, Al, Fe and Cu were significantly correlated to each other, reflecting their high affinity to the colloidal aromatic phase of DOC. During dry periods, particulate TM accumulate on canopy (Rodrigo and Avila, 2002). This induces increased concentrations and fluxes under canopy for Al, Fe, Pb and Cu (Petty and Lindberg, 1990; Hou et al., 2005b; Rodrigo et al., 2003). Dissolution of particles can be a sink of protons and can partly explain proton consumption by the canopy (Lindberg et al., 1986). Since complete complexation of Al, Fe, Cu and Pb by DOC was observed in TF, DOC might also have acted as a solubilising agent of some particles, increasing colloidal fluxes in TF. This has been suggested by Hou et al. (2005b), who observed TM leaching from soil particles in contact with TF.

Pb, Cd and Sb were well correlated in BD and might have a similar origin. In TF they had a different behavior. While Pb flux was increased in TF and was associated to colloidal DOC, Sb flux was also increased but in a truly dissolved form, since Sb was not associated with DOC. Cd, which was more labile, interacted with vegetation. As a result, its flux was not increased in TF.

Element dynamics in forest ecosystems did not depend on their origin but on their chemical properties and affinity for DOC in throughfall.

5. Conclusion

This study of trace metal deposition in open field bulk deposition and its interaction with forest cover provides new results on present-day trace metal atmospheric pollution in forest ecosystems. French forest ecosystems undergo anthropogenic inputs of TM. Throughfall composition is highly influenced by forest cover. TM concentrations and fluxes are modified in relation to their chemical properties and role for the biosphere. In throughfall, Mn, Sb, Cd, Zn and Ni are mainly found in the truly dissolved fraction, whereas Al, Pb and Fe are found in the fine colloidal fraction, associated to colloidal DOC. Increased fluxes of Mn under canopy was supposed to be from canopy release, whereas direct assimilation of Cd, Zn and Ni was evidenced. Sb and elements which are in the form of colloidal organic complexes (Pb, Al, Fe), are highly enriched under canopy. Accumulation of dry particles and their consecutive dissolution by organic molecules are probable. Forest cover modifies atmospheric inputs both in quantitative and qualitative ways. Indeed, some fluxes might not be modified or even decreased (Zn, Ni, Cd), whereas some others might be considerably increased (Pb, Sb). Moreover, availability of these elements might also be modified, since particle dissolution is enforced by the high concentration of complexing DOC.

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